## MINNESOTA DEPARTMENT OF COMMERCE

Proposed Test Method for Determination of Fatty Acid Methyl Ester (FAME) Content in Blends of Biodiesel with Conventional Middle Distillate Fuels Using Fourier Transform Mid-infrared Spectroscopy with a Multivariate Partial Least Squares (PLS<sub>1</sub>)

Calibration Model<sup>1</sup>

### 1. SCOPE

- 1.1 This test method covers the quantitative determination of fatty acid methyl ester (FAME) content in blends of biodiesel with conventional middle distillate fuels using Fourier transform midinfrared (FTIR) spectroscopy with a multivariate analysis based upon a partial least squares ( $PLS_1$ ) calibration model. The test method is applicable to fatty acid methyl ester concentrations from 0.1 to 30.0 volume percent.
- 1.2 This test method applies to fuels composed of biodiesel (B100) Grades S15 and S500, defined by Specification D 6751, blended with diesel fuel oils, defined by Specification D 975, Grades 1-D, 2-D, and low sulfur 1-D and 2-D.
  - 1.3 SI units of measurement are preferred and used throughout this standard.
- 1.4 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.

### 2. REFERENCED DOCUMENTS

- 2.1 *ASTM Standards*:
  - D 975 Standard Specification for Diesel Fuel Oils<sup>2</sup>
  - D 1298 Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method<sup>2</sup>
  - D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter<sup>3</sup>
  - D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products<sup>3</sup>
  - D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products<sup>3</sup>
  - D 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards<sup>3</sup>

<sup>&</sup>lt;sup>1</sup> This proposed test method has been presented for consideration to an ASTM work group on biodiesel blend quantization methodology.

<sup>&</sup>lt;sup>2</sup> Annual Book of ASTM Standards, Vol. 05.01.

<sup>&</sup>lt;sup>3</sup> Annual Book of ASTM Standards, Vol. 05.02.

- D 5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products<sup>4</sup>
- D 6751 Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels<sup>5</sup>
- E 168 Practices for General Techniques of Infrared Quantitative Analysis<sup>6</sup>
- E 168 Practices for General Techniques of Infrared Quantitative Analysis<sup>6</sup>
- E 1655 Practices for Infrared Multivariate Quantitative Analysis<sup>6</sup>
- E 2056 Practice for Qualifying Spectrometers and Spectrophotometers for Use in Multivariate Analyses, Calibrated Using Surrogate Mixtures<sup>6</sup>

### 3. TERMINOLOGY

- 3.1 *Definitions:*
- 3.1.1 *Multivariate calibration*—A process for creating a calibration model in which multivariate mathematics is applied to correlate the absorbance measured for a set of calibration samples to reference component concentrations or property values for the set of samples.
- 3.1.1.1 *Discussion*—The resultant multivariate calibration model is applied to the analysis of spectra of unknown samples to provide an estimate of the component concentration or property values for the unknown sample.
- 3.1.1.2 *Discussion*—The multivariate calibration algorithm employed in this method is Partial Least Squares ( $PLS_1$ ).
  - 3.1.2 *Biodiesel,n*—As defined in D 6751 03a, section 3.1.1.
  - 3.1.3 Biodiesel blend, BXX, n—As defined in D 6751 03a, section 3.1.2.
  - 3.1.4 *Biodiesel fuel, n*—synonym for *biodiesel*.

#### 4. SUMMARY OF TEST METHOD

- 4.1 A sample composed of biodiesel blended with middle distillate fuel is introduced into a liquid sample cell. A beam of infrared light is imaged through the sample onto a detector, and the detector response is determined. Wavelengths of the spectrum that correlate highly with fatty acid methyl ester or interferences are selected for analysis by mathematically selecting areas of the whole spectrum. A partial least squares multivariate mathematical analysis converts the detector response for the selected areas of the spectrum of an unknown to a volume percent concentration of fatty acid methyl ester.
- 4.2 For precision, two calibration models are employed. One covering low-level biodiesel blends (0 to 5 volume %) and the other, high-level biodiesel blends (5 to 30 volume %).

<sup>&</sup>lt;sup>4</sup> Annual Book of ASTM Standards, Vol. 05.03.

<sup>&</sup>lt;sup>5</sup> Annual Book of ASTM Standards, Vol. 05.04.

<sup>&</sup>lt;sup>6</sup> Annual Book of ASTM Standards, Vol. 03.06.

## 5. SIGNIFICANCE AND USE

- 5.1 Biodiesel, as a fuel commodity, has experienced increasing use, primarily as a value-added blending component with middle distillate fuel. Growing concern for energy independence and a reduction of fossil fuel pollutants, along with Federal and State sponsored incentives and/or mandates, will likely foster a continuance of this marketplace trend. Biodiesel blends may gain additional prominence as ultra-low sulfur diesel enters the marketplace because of lubricity benefits provided by biodiesel.
- 5.2 Fatty acid **methyl** ester (FAME) is the dominant composition of biodiesel in current commercial production, domestically and abroad. This test method is viable for FAME derived from all commonly used varieties of virgin oil and/or recycled oil feedstock if due attention is given to correspondence between the oil sources represented in calibration standards with that of the samples tested.
  - 5.3 This test method is fast, uncomplicated to perform and inexpensive.
- 5.4 Biodiesel blend concentration (BXX) is commonly denoted in fuel contracts and is certain to be specified in existing and forthcoming incentive programs and legislative mandates.
- 5.5 This test method is applicable to quality control of FAME based biodiesel blending and distribution, and for monitoring and enforcement of biodiesel blend specifications.

### 6. INTERFERENCES

6.1 The primary potential spectral interferences are from biodiesel oil feedstocks and cold flow additives. Matrix effects that are related to compositional differences between biodiesel or middle distillate product streams must also be considered possible. Proper choice of the apparatus, proper design of a calibration matrix, and proper utilization of the multivariate calibration technique can minimize these interferences

### 7. APPARATUS

7.1 Fourier Transform Mid-IR Spectrometer—The type of apparatus suitable for use in this test method employs an IR source, a liquid attenuated total internal reflection cell, a scanning interferometer, a detector, an A-D converter, a microprocessor, and a method to introduce the sample. The following performance specifications (through the ATR cell) must be met:

scan range	4000 to 600 cm <sup>-1</sup>
resolution	4 cm <sup>-1</sup>
S/N at 1746 cm <sup>-1</sup>	>300:1 RMS

The signal to noise level will be established by taking a single beam spectrum using air or nitrogen as the reference and declaring that spectrum as the background. The background single beam spectrum obtained can be the average of multiple FTIR scans, but the total collection time shall not exceed 60 s. If interference from water vapor or carbon dioxide is a problem, the instrument shall be purged with dry air or nitrogen. A subsequent single beam spectrum shall be taken under the same conditions and ratioed to the background spectrum. The RMS noise of the ratioed spectra, the 100 % line, shall not exceed 0.3 % transmittance in the region from 1765 to  $1725 \text{ cm}^{-1}$ .

7.2 Attenuated Total Reflectance (ATR) Cells, shall have the following specifications:

ATR element material ZnSe

beam condensing optics conical non-focusing optics integral to cell body element configuration circular cross section with coaxial conical ends

Cone half angle 60°

element length 1.55 in.
element diameter 0.125 in.
angle of incidence at sample interface 53.8°

maximum range of incidence angles ± 1.5°

standard absorbance (1428 cm<sup>-1</sup> band of acetone)  $0.38 \pm 0.02$  AU

material of construction 316 stainless steel

Seals Chemraz or Kalraz o-rings

#### 8. REAGENTS AND MATERIALS

- 8.1 Standards for Calibration, Qualification, and Quality Control Check Standards—As this method is intended to quantify FAME content in commercial biodiesel blends there are no high purity standard chemical reference materials that are appropriate for development of multivariate calibration models.
- 8.2 B100 (i.e. neat biodiesel) used for calibration, qualification and quality control standards must be D 6751 compliant and, so far as possible, should be representative of the biodiesel component in blends to be analyzed (e.g., rape seed oil, soybean oil, waste grease, etc.).
- 8.3 Middle distillate fuel used for calibration, qualification and quality control standards must be D 975 compliant, free of biodiesel and/or biodiesel oil precursor, and so far as possible should be representative of petroleum base stocks anticipated for blends to be analyzed (i.e., crude source, 1D, 2D, blends, winter/summer cuts, etc).

### 9. HAZARDS

9.1 Caution should be exercised in servicing Fourier transform spectrophotometers because of the risk associated with the laser that is used for determining the position of the interferometer scanning mirror.

### 10. SAMPLING, TEST SPECIMENS, AND TEST UNITS

- 10.1 General Requirements
- 10.1.1 Fuel samples to be analyzed by the test method shall be sampled using procedures outlined in Practices D 4057, or D 4177, where appropriate. Do not use "Sampling by Water Displacement." FAME is more water-soluble than the hydrocarbon base in a biodiesel blend.

- 10.1.2 Protect samples from excessive temperatures prior to testing. This can be accomplished by storage at room temperature (i.e. 18 to 27°C).
- 10.1.3 Do not test samples stored in leaky containers. Discard and obtain a new sample if leaks are detected.
  - 10.2 Sample Handling During Analysis:
- 10.2.1 When analyzing samples with the mid infrared apparatus, the sample must be between a temperature of 18 to 27°C. Equilibrate all samples to the temperature of the laboratory (18 to 27°C) prior to analysis by this test method.
- 10.2.2 After analysis, if the sample is to be saved, reseal the container and store the sample at 18 to 27°C.

# 11. CALIBRATION AND QUALIFICATION OF THE APPARATUS

- 11.1 Before use, the instrument must be calibrated according to the procedure described in Annex A1. This calibration can be performed by the instrument manufacturer prior to delivery of the instrument to the end user. If, after maintenance, the instrument calibration is repeated, the qualification procedure must also be repeated.
- 11.2 Before use, the instrument must be qualified according to the procedure described in Annex A1. The qualification need only be carried out when the instrument is initially put into operation, recalibrated, or repaired.

## 12. QUALITY CONTROL CHECKS

- 12.1 Confirm the calibration of the instrument each day it is used by measuring the biodiesel concentration using the procedure outlined in Section 13 on at least one quality control sample of known biodiesel content. The preparation of samples with known biodiesel concentration is described in 12.1.1 and 12.1.2.
- 12.1.1 Standard(s) of known biodiesel concentration shall be made up by mass according to A1.1 and converted to volume % using the measured density as outlined in Section 13. At least one standard shall be made up that is nominally 2.0 volume %. Additional standards may also be prepared and used for quality control checks.
- 12.1.2 Standard(s) should be prepared in sufficient volume to allow for a minimum of 30 quality control measurements to be made on one batch of material. Package and/or store quality control samples to ensure that all analyses of quality control samples from a given lot are performed on essentially identical material.
- 12.2 If the biodiesel volume % value estimated for the quality control sample prepared at 2.0 volume % biodiesel differs from the known value by more than 0.20 volume %, then the measurement system is out-of-control and cannot be used to estimate biodiesel concentrations until the cause of the out-of-control behavior is identified and corrected.
- 12.3 If correction of out-of-control behavior requires repair to the instrument or recalibration of the instrument, the qualification of instrument performance described in A1.3 shall be performed before the system is used to measure biodiesel content on samples.

## 13. PROCEDURE

- 13.1 Equilibrate the samples to between 18 to 27°C before analysis.
- 13.2 Clean the sample cell. If a separate baseline using the empty cell is required, and if there is residual fuel in the sample cell, remove the fuel by flushing the cell and inlet-outlet lines with enough pentane to ensure complete washing. Evaporate the residual pentane with either dry air or nitrogen.
- 13.3 If needed, obtain a baseline spectrum in the manner established by the manufacturer of the equipment.
- 13.4 Prior to the analysis of unknown test samples, establish that the equipment is running properly by collecting the spectrum of the quality control standard(s), by analyzing the spectrum with the calibration model, and by comparing the estimated biodiesel concentration to the known value for the QC standard(s).
- 13.5 Introduce enough standard to the cell to ensure that the cell is washed a minimum of three times with the standard solution.
- 13.6 Introduce the unknown fuel sample in the manner established by the manufacturer. Introduce enough of the fuel sample to the cell to ensure the cell is washed a minimum of three times with the fuel.
  - 13.7 Obtain the spectral response of the fuel sample.
- 13.7.1 Acquire the digitized spectral data for the fuel sample over the frequency region from  $4000 \text{ cm}^{-1}$  to  $600 \text{ cm}^{-1}$ .
- 13.8 Determine the biodiesel concentration (volume %) according to the appropriate calibration equation developed in Annex A1.
- 13.8.1 Determine the biodiesel concentration using the PLS<sub>1</sub> calibration models developed in A1.2.4 by following the steps outlined as follows.
- 13.8.1.1 Baseline correct the spectrum using a linear base-line fit to the absorbances measured from the left minima between 1870 and 1810 cm<sup>-1</sup> to the right minima between 684 and 638 cm<sup>-1</sup>.
- 13.8.1.2 Estimate the biodiesel concentration in the fuel sample by applying the low calibration (see A1.2.5) to the baseline corrected spectrum in the region of 1794 to 670 cm<sup>-1</sup>.
- 13.8.1.3 If the estimated biodiesel concentration (determined in 13.8.1.2) is equal to or less than 5.00 volume %, determine the biodiesel concentration by applying the low calibration (see A1.2.5) to the baseline corrected spectrum in the region of 1794 to 670 cm<sup>-1</sup>.
- 13.8.1.4 If the estimated biodiesel concentration (determined in 13.8.1.2) is greater than 5.00 volume %, estimate the biodiesel concentration by applying the high calibration (see A1.2.6) to the baseline corrected spectrum in the region of 1794 to 670 cm<sup>-1</sup>.
- 13.8.1.5 If the value estimated by application of the high calibration (determined in 13.8.1.4) is less than or equal to 5.00 volume %, report the value determined by the low calibration (even if the value is greater than 5.00 volume %). For estimated values greater than 5.00 volume % (determined in 13.8.1.4), report the value obtained.

## 14. CALCULATION

14.1 Conversion to Volume % of Biodiesel—To convert the calibration and qualification standards to volume % use Eq 1.

$$V_b = M_b \left( D_f / \mathcal{D}_b \right) \tag{1}$$

where:

 $V_b$  = biodiesel volume %,

 $M_b$  = biodiesel mass %, and

 $D_f$  = relative density at 15.56°C of the calibration or qualification standard finished blend.

 $D_b$  = relative density at 15.56°C of the biodiesel component of calibration or the qualification standard. (Densities shall be determined by Practice D 1298 or Test Method D 4052.)

### 15. REPORT

- 15.1 Report the following information:
- 15.2 Volume % biodiesel by Test Method D XXXX, to the nearest 0.01%.

### 16. PRECISION AND BIAS

- 16.1 {Note: formulas below are placeholders pending interlaboratory round-robin tests.}
- 16.2 Repeatability—For biodiesel concentrations between 0.1 and 5.0 volume %, the difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test samples would, in the long run, and in the normal and correct operation of the test method, exceed the following values only in one case in twenty.

$$r = \{\text{intercept}\} + \{\text{slope}\} X$$
 (2)

where X is the biodiesel concentration determined.

16.3 Reproducibility for FTIR Instruments Using a PLS Calibration Instrument—For biodiesel concentrations between 0.1 and 5.0 volume %, the difference between two single and independent results obtained by different operators working in different laboratories on identical test samples would, in the long run, and in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

$$R = \{\text{intercept}\} + \{\text{slope}\} X \tag{3}$$

where *X* is the biodiesel concentration determined.

16.4 *Bias*—Since there is no accepted reference material suitable for determining bias for the procedure in this test method, no statement of bias is being made.

### 17. KEYWORDS

17.1 alternative fuel; biodiesel fuel; diesel fuel oil; fuel oil; renewable resource; infrared spectroscopy.

#### **ANNEX**

# (Mandatory Information)

## A1. Calibration and Qualification of the Apparatus

- **A1.1** Calibration Matrix—Calibration standards shall be prepared in accordance with Practice D 4307 or appropriately scaled for larger blends and Practice D 5854, where appropriate. Whenever possible, use blend components known to be fully compliant with D 975 (for base petroleum diesel components) and D 6751 (for B100 biodiesel components).
- A1.1.1 Calibration Matrices for FTIR Instruments Using a PLS Calibration— To obtain the best precision and accuracy of calibration, prepare two biodiesel calibration sets as set forth in Table A1.2 and Table A1.3. The first set (Set A) has 50 samples with biodiesel concentrations from 0 to 6.0 volume %. The second set (Set B) has at least 35 samples with biodiesel concentrations from 0 to 30 volume %. Each of the subsets in Set B shall have a minimum of seven samples with biodiesel concentrations evenly spaced over the range of 0 to 30 volume %.
- A1.1.1.1 Measure the density for each of the calibration standards according to either Test Method D 1298 or Test Method D 4052.
- A1.1.1.2 For each of the calibration standards, convert the mass % biodiesel to volume % biodiesel according to the equation presented in 13.1. If the densities of the calibration standards can not be measured, it is acceptable to convert to volume % using the densities of the individual components measured using Test Method D 1298 or Test Method D 4052.

### **A1.2** *Calibration:*

- A1.2.1 The instrument must be calibrated in accordance with the mathematics as outlined in Practices E 1655. This practice serves as a guide for the multivariate calibration of infrared spectrometers used in determining the physical characteristics of petroleum and petrochemical products. The procedures describe treatment of the data, development of the calibration, and qualification of the instrument.
- A1.2.2 Equilibrate all samples to the temperature of the laboratory (18 to 27°C) prior to analysis. Fill the sample cell with the calibration standards in accordance with Practices E 168 or in accordance with the manufacturer's instructions.
- A1.2.3 For each of the calibration standards, acquire digitized spectral data over the frequency region from 4000 cm<sup>-1</sup> to 600 cm<sup>-1</sup>. The infrared spectrum is the negative logarithm of the ratio of the single beam infrared spectrum obtained with a sample and the single beam FTIR spectrum with dry air (or nitrogen). Baseline correct the spectrum using a linear baseline fit to absorbances measured for the bandwidth between 1794 and 668 cm<sup>-1</sup> (e.g. set baseline to the left minima from 1870 to 1810 cm<sup>-1</sup> and the right minima from 684 to 638 cm<sup>-1</sup>).
  - A1.2.4 Using a PLS calibration, two separate calibrations will be developed.
- A1.2.5 Develop the first calibration (using samples over the range of 0 to 5 volume %), referred to as the low calibration, using spectra obtained from the samples in calibration Set A detailed in Table A1.1. This calibration relates the spectrum to the biodiesel concentration (volume %). Use baseline corrected data in the region of 1794 to 670 cm<sup>-1</sup> to develop the low calibration. Use mean centering and at least four latent variables in developing the model.

TABLE A1.1 Low Range Calibration: Training Set A (0 to 5 Volume %)

#	Vol. % FAME	Vol. % #2	Vol. % #1
1	0.0	100	0
2	0.5	100	0
3	1.0	100	0
4	2.0	100	0
5	2.5	100	0
6	3.0	100	0
7	3.5	100	0
8	4.0	100	0
9	4.5	100	0
10	5.0	100	0
11	5.5	100	0
12	6.0	100	0
13	0.0	75	25
14	0.5	75	25
15	1.0	75	25
16	2.0	75	25
17	2.5	75	25
18	3.0	75	25
19	3.5	75	25
20	4.0	75	25
21	4.5	75	25
22	5.0	75	25
23	5.5	75	25
24	6.0	75	25
25	0.0	50	50
26	0.5	50	50
27	1.0	50	50
28	2.0	50	50
29	2.5	50	50
30	3.0	50	50
31	3.5	50	50
32	4.0	50	50
33	4.5	50	50
34	5.0	50	50
35	5.5	50	50
36	6.0	50	50
37	0.0	0	100
38	0.5	0	100
39	1.0	0	100
40	2.0	0	100
41	2.5	0	100
42	3.0	0	100
43	3.5	0	100
44	4.0	0	100
45	4.5	0	100
46	5.0	0	100
47	5.5	0	100
48	6.0	0	100

TABLE A1.2 High Range Calibration: Training Set B (0 to 30 Volume %)

			<u> </u>
#	Vol. % FAME	Vol. % #2	Vol. % #1
1	0	100	0
2	5	100	0
3	10	100	0
4	15	100	0
5	20	100	0
6	25	100	0
7	30	100	0
8	0	75	25
9	5	75	25
10	10	75	25
11	15	75	25
12	20	75	25
13	25	75	25
14	30	75	25
15	0	50	50
16	5	50	50
17	10	50	50
18	15	50	50
19	20	50	50
20	25	50	50
21	30	50	50
22	0	0	100
23	5	0	100
24	10	0	100
25	15	0	100
26	20	0	100
27	25	0	100
28	30	0	100

### **NOTES:**

Volume % FAME columns in Tables A1.1 and A1.2 reference the concentration in the final biodiesel blend.

Volume % #1 and Volume % #2 columns reference only the relative concentrations of #1 and #2 diesel fuels making up the petroleum middle distillates used as the blend stock for the biodiesel blend standard.

- A1.2.6 Develop the second calibration (using samples over the range 0 to 30 volume %), referred to as the high calibration, using spectra obtained from all of the samples in calibration Set B as detailed in Table A1.2. This calibration relates the spectrum to the biodiesel concentration (volume %). Use baseline corrected data in the region of 1794 to 670 cm<sup>-1</sup> to develop the high calibration. Use mean centering and at least four latent variables in developing the model.
- **A1.3** Qualification of Instrument Performance—Once a calibration has been established, the individual calibrated instrument must be qualified to ensure that the instrument accurately and precisely measures biodiesel in the presence of typical compression-ignition engine fuel compounds that, in typical concentrations, present spectral interferences. This qualification need only be carried out when the instrument is initially put into operation, is recalibrated, or repaired.
- A1.3.1 Preparation of Qualification Samples—Prepare multi-component qualification standards of the biodiesel by mass according to Practices D 4307 (or appropriately scaled for larger blends), or D 5854, where appropriate. These standards shall be similar to, but not the same as, the mixtures established for the calibration set used in developing the calibration. Prepare the qualification samples so as to vary the concentrations of biodiesel and of the interfering components over a range that spans at least 95 % of that for the calibration standards. The numbers of required standards are suggested by Practices E 1655 and, in general, will be five times the number of independent variables in the calibration equation. For a four component PLS model a minimum of 20 qualification standards are required.
- A1.3.2 Acquisition of Qualification Data—For each of the qualification standards, measure the biodiesel concentration, expressed in volume %, according to the procedure established in Section 12. The adequacy of the instrument performance is determined following the procedures described in Practice E 2056.
  - A1.3.3 The standard error of qualification (SEQ) is calculated as follows:

$$SEQ = \sum (\hat{y}_i - y_i)^2 / q \sqrt{\frac{q}{i-1}}$$

where:

q = number of surrogate qualification mixtures,

 $y_i$  = component concentration for the i<sup>th</sup> qualification sample, and

 $\hat{y}_i$  = estimate of the concentration of the i<sup>th</sup> qualification sample.

- A1.3.3.1 An F value is calculated by dividing SEQ by PSEQ (the pooled standard error of qualification for the round robin instruments). The F value is compared to a critical F value with q degrees of freedom in the numerator and DOF(PSEQ) degrees of freedom in the denominator. Values of PSEQ and DOF(PSEQ) are given in Table A1.6, and the critical F values in Table A1.7.
- A1.3.3.2 If the F value is less than or equal to the critical F value from the table, then the instrument is qualified to perform the test.
- A1.3.3.3 If the F value is greater than the critical F value from the table, then the instrument is not qualified to perform the test.

**TABLE A1.4 Pooled Standard** 

### **Error of Qualification**

PSEQ	0.0555
DOF(PSEQ)	306

TABLE A1.5 Critical F Value

17.12.22.71.110.01.11.00	
	Numerator q
Denominator DOF(PSEQ)	306
20	1.60
25	1.54
30	1.50
35	1.46
40	1.43
45	1.41
50	1.39

{Note: Values in Table A1.5 are temporary example placeholders pending results of a formal precision and bias interlaboratory round-robin study.}

# Modeling parameters from calibration.tdf (Grams 32 Training Data File): \*\*\*\* DATAINFO \*\*\*\* **Description:** Tot. Spectra: 52 Tot. Constit: 1 Tot. Points: 1765 X Unit Type: 1 Y Unit Type: 2 First X : 4002.54 Last X : 599.9 \*\*\*\* EXPINFO \*\*\*\* **Experiment: Default Experiment** Num. Spectra: 52 Num. Constit: 1 Calibration: PLS1 Regions: 1 Factor Sets: 1 Cal Factors: 9 **Preprocessing Used: Mean Center Manual Baseline** Manual Baseline Used: 1869.98 Left: 1809.98 Min 683.841 637.687 Min Right: \*\*\*\* BANDS \*\*\*\* Left Right Space **Points** Group 1793.91 669.341 1 584 Avg \*\*\*\* CNAME \*\*\*\* **Biodiesel**

FIG. 1. Example PLS<sub>1</sub> calibration parameters from a Grams 32 training data file (.tdf) printout.

# **Computation Worksheet for Biodiesel Calibration Standards**

Sample I.D. # ==>		Tar	get Volume of Bxx I	Blend Standard =	250
Neat (B100)	Targeted	Volume	Measured	Targeted	Measured
Biodiesel	Volume%	in mL	Density (kg/L)	Mass (g)	Mass (g)
Component	4	10	.8812	8.8120	
Cold Temperature	Targeted	Volume	Measured	Targeted	Measured
Performance or	Volume%	in μL	Density (kg/L)	Mass (g)	Mass (g)
Other Additive	v ordine / o	шиг	Density (kg/L)	171455 (g)	mass (g)
Other Muditive					
Diesel Blend	Targeted	Volume	Measured	Targeted	Measured
Components	Volume%	in mL	Density (kg/L)	Mass (g)	Mass (g)
Diesel (Part A)	50	120	0.8654	103.8480	
Diesel (Part B)	50	120	0.8348	100.1770	
			for all Components i		250.0000
These results			ing deviations from		4.0000
			esel in the Finished I		
	Computed	1 Mass % Biodic	esel in the Finished I	siend Standard =	4.1403
These result	s are to be used if th	ere were weighi	ng deviations from T	Targeted Mass	
	Actual V	olume % Biodio	esel in the Finished I	Blend Standard =	?
	Actua				

FIG. 2. Screen Capture of an Excel® worksheet that calculates component weights for biodiesel blend calibration standards.

#### **Instructions for using this worksheet:**

Green cells are input fields and are unprotected. Yellow cells are result fields and are protected.

Enter total targeted volume of biodiesel standard.

Enter targeted volume % for biodiesel component. Enter measured density of biodiesel component.

Enter targeted volume % for additive component. Enter measured density of additive component.

Enter targeted volume % of diesel component A in the total composition of the diesel blend alone (i.e. enter 100 if A is the sole diesel component). Enter the measured density of diesel component A.

If diesel component A is less that 100%, enter the measured density for component B (the targeted volume % for diesel component B is computed automatically as the remainder of 100 minus A)

Weigh in the selected biodiesel blend components based on the computed target weights. Record the ACTUAL mass measurements obtained for ALL the components if there were ANY weighing errors. Read the actual volume % and mass % biodiesel in the standard from the final results fields of the appropriate table with regard to weighing error.

